Multiple quantum NMR dynamics in pseudopure states

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Abstract
We investigate numerically the multiple quantum (MQ) NMR dynamics in systems of nuclear spins 1/2 coupled by dipole–dipole interactions in the case of the pseudopure initial state. Simulations of the MQ NMR with real molecular structures such as six dipolar-coupled proton spins of benzene, hydroxyl proton chains in calcium hydroxyapatite, and fluorine chains in calcium fluorapatite open the way to experimental NMR testing of the obtained results. It was found that multiple-spin correlations are created faster in such experiments than in the usual MQ NMR experiments and can be used for the investigation of many-spin dynamics of nuclear spins in solids.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The method of multiple quantum nuclear magnetic resonance (MQ NMR) in solids [1] is a powerful tool for the investigation of structure and spin dynamics in solids [2]. Significant progress has been made in the simplification of ordinary NMR spectra [3]. Recently, higher order MQ NMR experiments have been utilized to address one of the fundamental issues in quantum information processing, the preparation of the pseudopure state [4]. A quantum computation includes, as an initial step, preparation of the input state [5]. Conveniently, the quantum algorithms start with a pure ground state where populations of all states except the ground state are equal to zero. The realization of a pure state in a real quantum system, such as a spin system, requires extremely low temperatures and very high magnetic fields. To overcome this problem, a so-called 'pseudopure' state was introduced [6, 7]. The density matrix of the spin system in this state can be partitioned into two parts. The first part of the matrix is a scaled unit matrix, and the second part corresponds to a pure state. The scaled unit matrix does not contribute to observables, and it is not changed by unitary evolution transformations. Therefore, the behavior of a system in the pseudopure state is exactly the same as it would be in the pure state.

Recently, it has been suggested [8, 9] to consider the dipolar ordered state as the initial state for such experiments. As a result of using the dipolar ordered initial condition, many-spin clusters and correlations appear faster [8, 9] than

in the ordinary MQ NMR experiments [1] in solids and some peculiarities of multiple quantum (MQ) dynamics can be investigated with these experiments.

In the present paper we consider MQ NMR dynamics when the initial condition is determined by the pseudopure state. Our motivation for performing this work is defined first of all by the fact that the many-spin correlations are created faster in such experiments than in standard MQ NMR methods and can be used for the investigation of many-spin dynamics of nuclear spins in solids. We consider dynamics of MQ NMR in systems prepared in the pseudopure state and calculate the resulting signal in MQ experiments. Note that it is not necessary to make any changes in the scheme of the standard experiment in order to obtain non-zero signals of MQ coherences in the pseudopure state. Computer simulations of such experiments for six spin rings and eight spin linear chains are presented.

2. MQ NMR with the initial pseudopure state

We consider a system of nuclear spins ($s = 1/2$) coupled by the dipole–dipole interaction (DDI) in a strong external magnetic field $\vec{H}_0$ which is directed along the z axis. The secular part of the DDI Hamiltonian [10] has the following form

$$\mathcal{H}_{dz} = \sum_{j<k} D_{jk} \left[I_{jz} I_{kz} - \tfrac{1}{4} \left(I_j^+ I_k^- + I_j^- I_k^+ \right) \right], \quad (1)$$

where $D_{jk} = \frac{\gamma^2 \hbar}{r_{jk}^3}(1 - 3\cos^2\theta_{jk})$ is the coupling constant between spins j and k, γ is the gyromagnetic ratio, r_{jk} is the distance between spins j and k, θ_{jk} is the angle between the internuclear vector $\overrightarrow{r_{jk}}$ and the external magnetic field. $I_{j\alpha}$ is the projection of the angular spin momentum operator on the axis $\alpha (\alpha = x, y, z)$; I_j^+ and I_j^- are the raising and lowering operators of spin j.

There are many pulse sequences exciting MQ coherences during the preparation period. For a dipolar-coupled spin system, the multipulse sequence with an eight-pulse cycle [1] is known to be very efficient. The basic scheme of the standard MQ NMR experiments consists of four distinct periods of time: preparation, evolution, mixing, and detection [1]. In the rotating reference frame [10] the average Hamiltonian describing the MQ dynamics at the preparation period can be presented as [1]

$$\mathcal{H}_{\mathrm{MQ}} = \mathcal{H}^{(2)} + \mathcal{H}^{(-2)}, \tag{2}$$

where $H^{(\pm 2)} = -\frac{1}{4}\sum_{j<k} D_{jk} I_j^{\pm} I_k^{\pm}$. Then the evolution period without any pulses follows. The density matrix of the spin system, $\rho(\tau)$, at the end of the preparation period is

$$\rho(\tau) = U(\tau)\rho(0)U^+(\tau), \tag{3}$$

where $U(\tau) = \exp(-i\tau(H^{(2)} + H^{(-2)}))$ is the evolution operator on the preparation period and $\rho(0)$ is the initial density matrix of the system. The transfer of the information about MQ coherences to the observable magnetization occurs during the mixing period. Usually the thermodynamical equilibrium density matrix is used as the initial one for MQ NMR experiments. In the high temperature approximation the equilibrium density matrix takes the form: $\rho(0) = I_z$. Here we consider MQ NMR dynamics with the initial pseudopure state when the density matrix can be described as:

$$\rho(0) = |1\rangle_1 \otimes |1\rangle_2 \otimes \cdots \otimes |1\rangle_N, \tag{4}$$

where $|1\rangle_k$ represents a kth spin that is up and N is the number of spins in the system. The method of creating the highly polarized spin states (4) in clusters of coupled spins was described previously [4, 11]. It is based on filtering multiple quantum coherence of the highest order, followed by a time-reversal period and partial saturation. It is convenient to expand the density matrix, $\rho(\tau)$, at the end of the preparation period of the MQ NMR experiment as [12]

$$\rho(\tau) = \sum_n \rho_n(\tau), \tag{5}$$

where the term $\rho_n(\tau)$ is responsible for the MQ coherences of the nth order. One can find

$$e^{-i\delta I_z t}\rho_n(\tau)e^{i\delta I_z t} = e^{-in\delta t}\rho_n(\tau). \tag{6}$$

On the mixing period the spin system is irradiated with a sequence of pulses shifted on a $\pi/2$-phase regarding the pulses of the preparation period [1]. As a result, the average Hamiltonian describing the evolution of the spin system on the mixing period changes sign to be opposite to the sign of the

Hamiltonian (2), and the evolution operator, $U(\tau)$, is replaced by the operator $U^+(\tau)$. Starting with the initial conditions (4), the density matrix, $\rho(t)$, after the three periods of the standard MQ NMR experiment can be written as

$$\rho(t) = U^+(\tau)e^{-i\delta t_1 I_z}\rho(\tau)e^{i\delta t_1 I_z}U(\tau), \tag{7}$$

where $\rho(\tau)$ is the density matrix at the end of the preparation period according to equation (3) and $t = 2\tau + t_1$, δ is the frequency offset on the evolution period of duration t_1 which is a result of applying the time proportional phase incrementation (TPPI) method [1]. The transfer of the information about MQ coherences to the observable magnetization occurs during the mixing period. The last unitary transformation in (7) with operator $U(\tau)$ describes this period. The resulting signal after the mixing period, the longitudinal magnetization, $M_z(t)$, is

$$M_z(t) = \mathrm{Tr}\{\rho(t)I_z\}. \tag{8}$$

Using equations (3) and (7) and the initial condition (4) it is convenient to present the formula (8) for the longitudinal magnetization, $M_z(t)$, as follows

$$M_z(t) = \mathrm{Tr}\{e^{-i\delta I_z t}\rho(\tau)e^{i\delta I_z t}\rho_{\mathrm{MQ}}(\tau)\} \tag{9}$$

where

$$\rho_{\mathrm{MQ}}(\tau) = U(\tau)I_z U^+(\tau), \tag{10}$$

coincides with the density matrix at the end of the preparation period of the standard MQ NMR experiment with the thermodynamical equilibrium density matrix as the initial condition at the high temperature approximation [1]. The density matrix $\rho_{\mathrm{MQ}}(\tau)$ can be represented in the following form [12]

$$\rho_{\mathrm{MQ}}(\tau) = \sum_n \rho_n^{\mathrm{MQ}}(\tau) \tag{11}$$

where the term $\rho_n^{\mathrm{MQ}}(\tau)$ is responsible for the MQ coherences of nth order and satisfies the relationship of equation (6). By using equations (6), (7), and (9) one can rewrite the expression for the observable signal in terms of the intensities of MQ coherences

$$M_z(t) = \sum_n e^{-in\delta t} J_n(\tau) \tag{12}$$

where $J_n(\tau)$ are the normalized intensities of MQ coherences and

$$J_n(\tau) = 2\mathrm{Tr}\left\{\rho_n(\tau)\rho_{-n}^{\mathrm{MQ}}(\tau)\right\}\bigg/N. \tag{13}$$

One can find from equation (13) that

$$J_n(\tau) = J_{-n}(\tau). \tag{14}$$

It is well known that in the usual MQ NMR experiments, the sum of the intensities of all MQ coherences does not depend on time $\sum_n J_n(\tau) = 1$. This is also right for the MQ NMR in the pseudopure state.
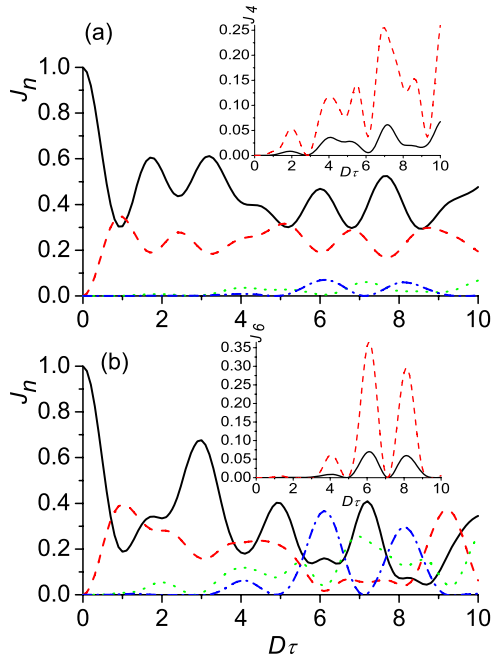
Figure 1. The time dependence of the intensities of the MQ coherences in a ring of six spins coupled by the DDI: (a) the thermal equilibrium initial state and (b) the pseudopure initial state (4). Black solid line: intensities of the zeroth order coherence J_0. Red dashed line: intensities of the second order coherence J_2. Green dotted line: intensities of the fourth order coherence J_4. Blue dashed-dotted line: intensities of the sixth order coherence J_6. The insets show that the MQ coherences of fourth (a) and sixth (b) orders in the pseudopure state (red dashed line) appear little earlier than in the usual MQ NMR (black solid line).

Figure 2. The time dependence of the intensities of the MQ coherences in a linear chain of eight spins coupled by the DDI: (a) the thermal equilibrium initial state and (b) the pseudopure initial state (4). Black solid line: intensities of the zeroth order coherence J_0. Red dashed line: intensities of the second order coherence J_2. Green dotted line: intensities of the fourth order coherence J_4. Blue dashed-dotted line: intensities of the sixth order coherence J_6. The insets show that the MQ coherences of fourth (a) and sixth (b) orders in the pseudopure state (red dashed line) appear a little earlier than in the usual MQ NMR (black solid line).

3. The numerical analysis of the time evolution of MQ coherences in the pseudopure state

We restrict ourselves to numerical simulations of MQ NMR dynamics of one-dimensional systems. For example, quasi-one-dimensional six dipolar-coupled proton spins of a benzene molecule [4] and hydroxyl proton chains in calcium hydroxyapatite $Ca_5(OH)(PO_4)_3$ [13] and fluorine chains in calcium fluorapatite $Ca_5F(PO_4)_3$ [13] are suitable objects to study MQ dynamics in pseudopure states. The numerical calculations were performed for MQ NMR dynamics of linear chains and rings of 6 and 8 spins. The DDI coupling constant of the nearest neighbors is chosen to be $D_{j,j+1} = D = 1 s^{-1}$. Then the coupling constants of spins j and k are $D[\frac{\sin(\pi/N)}{\sin(\pi(j-k)/N)}]^3$ for the ring and $D/|j-k|^3$ for the chain, respectively. In order to compare the results of the numerical simulations with the analogous ones for the ordinary MQ NMR dynamics, we introduce the normalized intensities of MQ coherences for the n order, $J_n^{\mathrm{ord}}(\tau)$ [1]

$$J_n^{\mathrm{ord}}(\tau) = \mathrm{Tr}\left\{\rho_n^{\mathrm{MQ}}(\tau)\rho_{-n}^{\mathrm{MQ}}(\tau)\right\}/\mathrm{Tr}\{I_z^2\}. \qquad (15)$$

The dependences of the intensities of MQ coherences on the dimensionless time, $t = D\tau$, of the preparation period in a spin ring containing six spins are presented in figure 1 for both initial states, equilibrium (a) and pseudopure (b). One can compare the intensities of MQ coherences in the suggested
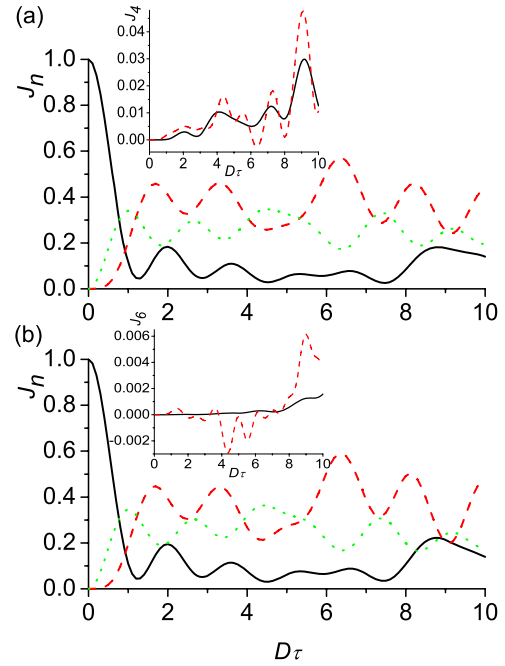
experiment with the standard ones. It is evident that the suggested method can be considered as a useful addition to the standard MQ NMR method. Figure 1 demonstrates that the suggested method yields the intensities of MQ coherences of the fourth and six orders which are several times higher than the analogous coherence in the standard MQ NMR experiment. It is clear from the insets of figure 1 that MQ coherences of the fourth and sixth orders, obtained with the initial condition (4), appear a little earlier than in the usual MQ NMR in a ring of six spins. For example, for the pseudopure state at time $D\tau = 2$ the MQ intensity of the fourth order coherence is 0.05 (red dashed line) while for the usually used initial condition up to $D\tau = 3$ the intensity J_4 is close to zero (black solid line). A tendency for faster growth of MQ coherences of high orders takes place also for the linear chain containing eight spins (figure 2). This peculiarity is connected with the initial pseudopure state (4). As a result, many-spin clusters and correlations connected with MQ coherences appear faster than in the standard MQ NMR with the initial condition, $\rho(0) = I_z$. The numerical calculations confirm also the results obtained in section 2. In particular, the growth of MQ coherences occurs in accordance with equation (14).

One can see from figure 2 that the observable intensities of the fourth and sixth orders in the linear chain containing eight spins can be negative in contrast to the ordinary MQ NMR experiments at high temperatures [1, 12, 14]. At the same time, it was shown [15] that the intensities of MQ coherences can be

negative in the standard NMR experiments at low temperatures and in the dipolar ordered state at high temperatures. In fact, in MQ NMR experiments the observable quantity is the longitudinal magnetization modulated by rf pulses. The distinct frequency components of the magnetization can have an arbitrary sign.

4. Conclusions

The MQ NMR method for the detection of MQ coherences starting from the pseudopure state is proposed. Investigations of MQ NMR dynamics in the pseudopure states can be considered as a supplementary method which complements the usual NMR in order to study structures and dynamical processes in solids. Many-spin clusters and many-spin correlations are created faster in such experiments than in the usual MQ NMR with the initial equilibrium condition without any correlation between the spins. In this paper we focused on simple one-dimensional examples but the physical picture obtained here is not limited to performing simulations and experiments in two-dimensional and three-dimensional systems will open new ways for the study of many-spin systems.

Acknowledgment

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